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5-Chloro-2-methoxyanilinium nitrate

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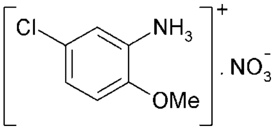
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.109; data-to-parameter ratio = 16.5.

The title salt, $C_7H_9ClNO^+\cdot NO_3^-$, exhibits extensive hydrogen bonding between the ammonium functional group and the nitrate anion. A two-dimensional network of bifurcated N—H$\cdots$O hydrogen bonds generates corrugated layers in the *bc* plane. The organic molecules are stacked in a parallel orientation as a result of π–π interactions, with an inter-ring distance of 3.837 Å.

Related literature

For related literature, see: Abid *et al.* (2007); Aloui *et al.* (2002); Desiraju & Steiner (1999); Hemissi *et al.* (2005); Jayaraman *et al.* (2002); Ouslati & Ben Nasr (2006); Steiner (2002); Kefi *et al.* (2007).



Experimental

Crystal data

$C_7H_9ClNO^+\cdot NO_3^-$
M_r = 220.61
Monoclinic, $P2_1/c$
a = 10.681 (2) Å
b = 9.474 (3) Å
c = 9.802 (3) Å
β = 102.38 (3)°
V = 968.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 293 (2) K
0.2 × 0.18 × 0.16 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: none
4244 measured reflections
2125 independent reflections
1409 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
2 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.109
S = 1.02
2125 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H1$\cdots$O1^{i}	0.89	2.08	2.967 (3)	173
N2—H1$\cdots$O2^{i}	0.89	2.57	3.103 (3)	120
N2—H2$\cdots$O1	0.89	2.04	2.927 (3)	171
N2—H2$\cdots$O3	0.89	2.38	3.043 (3)	131
N2—H3$\cdots$O2^{ii}	0.89	2.55	3.240 (3)	135
N2—H3$\cdots$O3^{ii}	0.89	2.07	2.939 (3)	165
C7—H9$\cdots$O2^{iii}	0.96	2.42	3.361 (4)	167

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2102).

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supplementary materials

Acta Cryst. (2008). E**64**, o801 [**doi:10.1107/S1600536808008805**]

5-Chloro-2-methoxyanilinium nitrate

H. Hemissi, **S. Abid** and **M. Rzaigui**

Comment

Hydrogen bonding is of intense interest because of their widespread occurrence in biological systems. So, it is very helpful to search simple molecules allowing to understanding the configuration and the function of some complex macromolecules.The hybrid compounds are rich in H-bonds and they could be used to this effect because of their potential importance in constructing sophisticated assemblies from discrete ionic or molecular building blocks due to its strength and directionality (Steiner. *et al.* 2002, Jayaraman, *et al.* 2002). In this work, the combination of 2-methoxy-5-chloroaniline and nitric acid has been chosen to elaborate the special hydrogen-bond pattern. The asymmetric unit of crystal structure, depicted in *ORTEP* drawing (Fig. 1), correspond to the formula unit $C_6H_9ClNO^+.NO_3^-$. The main feature of this atomic arrangement is the existence of thick inorganic corrugated layers spreading around *bc* plane (Fig. 2). Inside layer, each NO_3^- anion is linked to three organic groups through bifurcated N–H···O H-bonding. The N···O and H···O bond lengths are in the ranges of 2.927 (3)–3.240 (3) Å and 2.04–2.57 Å, respectively. The organic species interact also with a weak C–H···O hydrogen bond with H···O separation of 2.42 Å. These interactions are weaker than those observed otherwise (Ouslati *et al.* 2006, Kefi *et al.* 2007). The orientation of molecules in this framework is governed by a nearly regular triangular arrangement of 2-methoxy-5-chlorophenylammonium groups [N···N distances between nitrogen ammonium atoms are in the range of 5.597 and 5.857 Å, N···N···N angles range from 57.75 to 62.25°] (Fig. 3). As well as electrostatic and van der Waals forces and hydrogen bonds, aromatic π-π stacking interactions participate to define the crystal packing. Indeed, in the atomic arrangement of the title compound, the phenyl ring of the organic molecules are stacked in the parallel orientation with interplanar separation of 3.837 Å indicating there are π–π stacking interactions (Desiraju & Steiner, 1999). The –Cl, $–NH_3$ and $–OCH_3$ substituents form, respectively, different torsion angles with the benzene ring: Cl—C5—C6—C1 ((t1) = 178.71°), N2—C1—C2—C3 ((t2) = -179.74°) and C7—O4—C2—C3 ((t3) = 12.43°). (t1) and (t2) angle values show that the chloro and amino substituents are nearly coplanar with the aryl ring. The torsion angle (t3) value indicates that the methoxy group lies out the plane of the benzene ring. This conformation resembles that observed in other compounds (Abid *et al.* 2007, Aloui *et al.* 2002, Hemissi *et al.* 2005).

Experimental

An ethanolic 2-methoxy-5-chloroaniline solution (5 mmol, in 5 ml) was added to an aqueous HNO_3 solution (0.5 *M*). The obtained solution is evaporated during several days in ambient condition until the formation of single crystals of the title compound.

Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, [N–H = 0.89, C–H =0.96 Å (CH_3) with with U_{iso}(H) = 1.5Ueq and C–H =0.96 Å (Ar–H), with U_{iso}(H) = 1.5Ueq]

Figures

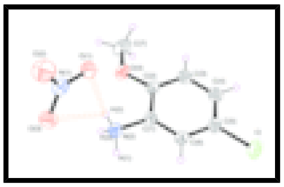

Fig. 1. *ORTEP-3* (Farrugia,(1999)) view of the title compound, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level, and H-atoms are shown as spheres with an arbitary radius.

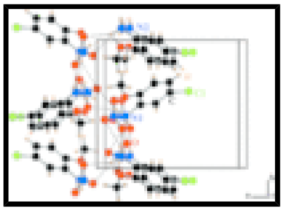

Fig. 2. A perspective view of the atomic arrangement of the title compound.

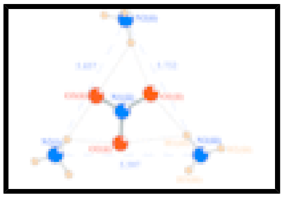

Fig. 3. Nitrate anion environment in the title compound. [Symmetry operators: (i) *x*, *y*, *z*; (ii) -*x*, *y* + 1/2, -*z* + 1/2; (iii) -*x*, -*y*, -*z*].

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Crystal data

$C_7H_9ClNO^+ \cdot NO_3^-$
$M_r = 220.61$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 10.681\ (2)$ Å
$b = 9.474\ (3)$ Å
$c = 9.802\ (3)$ Å
$\beta = 102.38\ (3)$°
$V = 968.8\ (5)$ Å^3
$Z = 4$

$F_{000} = 456$
$D_x = 1.513$ Mg m^{-3}
Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.1$–10.8°
$\mu = 0.39$ mm^{-1}
$T = 293\ (2)$ K
Prism, black
0.2 × 0.18 × 0.16 mm

Data collection

Enraf–Nonius TurboCAD4 diffractometer
Monochromator: graphite
non–profiled ω scans
Absorption correction: none
4244 measured reflections
2125 independent reflections
1409 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

$\theta_{max} = 27.0$°
$\theta_{min} = 2.9$°
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 0$
$l = -12 \rightarrow 12$
2 standard reflections
every 120 min
intensity decay: 5%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.2112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2125 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
129 parameters	$\Delta\rho_{min} = -0.42$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cl	0.39657 (5)	0.59783 (8)	0.79445 (7)	0.0703 (2)
N2	0.83926 (16)	0.40697 (19)	0.75239 (18)	0.0478 (4)
H2	0.8415	0.3375	0.6918	0.072*
H1	0.8331	0.3705	0.8344	0.072*
H3	0.9107	0.4579	0.7630	0.072*
O4	0.83237 (15)	0.55493 (16)	0.52279 (16)	0.0568 (4)
C1	0.72828 (18)	0.4973 (2)	0.6998 (2)	0.0387 (4)
C2	0.72905 (19)	0.5751 (2)	0.5790 (2)	0.0425 (5)
C3	0.6254 (2)	0.6618 (2)	0.5276 (2)	0.0530 (6)
H4	0.6241	0.7158	0.4481	0.064*
C4	0.5237 (2)	0.6682 (2)	0.5941 (2)	0.0532 (5)
H5	0.4537	0.7256	0.5585	0.064*
C5	0.52562 (19)	0.5906 (2)	0.7117 (2)	0.0465 (5)
C6	0.62876 (18)	0.5041 (2)	0.7675 (2)	0.0425 (5)
H6	0.6303	0.4523	0.8484	0.051*
C7	0.8528 (3)	0.6480 (3)	0.4147 (3)	0.0714 (7)
H7	0.7883	0.6316	0.3316	0.107*
H8	0.9360	0.6309	0.3957	0.107*

H9	0.8477	0.7441	0.4443	0.107*
O1	0.82176 (15)	0.19146 (16)	0.53507 (16)	0.0556 (4)
N1	0.88696 (17)	0.09358 (19)	0.60238 (19)	0.0484 (4)
O2	0.8812 (2)	−0.02617 (18)	0.5536 (2)	0.0835 (6)
O3	0.95687 (16)	0.12025 (18)	0.71720 (17)	0.0648 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0462 (3)	0.0888 (5)	0.0816 (5)	−0.0011 (3)	0.0262 (3)	−0.0182 (4)
N2	0.0487 (9)	0.0465 (10)	0.0493 (10)	0.0074 (8)	0.0128 (8)	0.0016 (8)
O4	0.0608 (9)	0.0616 (10)	0.0553 (9)	0.0042 (8)	0.0284 (8)	0.0059 (8)
C1	0.0394 (9)	0.0342 (10)	0.0416 (10)	0.0017 (8)	0.0067 (8)	−0.0040 (8)
C2	0.0474 (11)	0.0390 (10)	0.0426 (11)	−0.0011 (9)	0.0133 (9)	−0.0051 (9)
C3	0.0641 (14)	0.0486 (13)	0.0465 (12)	0.0072 (11)	0.0123 (10)	0.0052 (10)
C4	0.0518 (12)	0.0508 (13)	0.0539 (13)	0.0117 (10)	0.0043 (10)	−0.0034 (11)
C5	0.0389 (10)	0.0487 (12)	0.0525 (12)	−0.0016 (9)	0.0112 (9)	−0.0156 (10)
C6	0.0465 (11)	0.0410 (11)	0.0411 (11)	−0.0061 (9)	0.0122 (9)	−0.0044 (9)
C7	0.0947 (19)	0.0575 (15)	0.0752 (17)	−0.0137 (14)	0.0481 (15)	−0.0009 (13)
O1	0.0598 (9)	0.0502 (9)	0.0562 (9)	0.0115 (8)	0.0108 (7)	0.0016 (7)
N1	0.0526 (10)	0.0451 (10)	0.0522 (11)	−0.0002 (9)	0.0215 (9)	−0.0025 (9)
O2	0.1170 (16)	0.0446 (10)	0.0859 (13)	0.0093 (10)	0.0152 (12)	−0.0144 (10)
O3	0.0709 (11)	0.0675 (11)	0.0518 (10)	0.0030 (8)	0.0038 (8)	−0.0049 (8)

Geometric parameters (Å, °)

Cl—C5	1.744 (2)	C3—H4	0.9300
N2—C1	1.463 (2)	C4—C5	1.364 (3)
N2—H2	0.8900	C4—H5	0.9300
N2—H1	0.8900	C5—C6	1.388 (3)
N2—H3	0.8900	C6—H6	0.9300
O4—C2	1.349 (2)	C7—H7	0.9600
O4—C7	1.431 (3)	C7—H8	0.9600
C1—C6	1.370 (3)	C7—H9	0.9600
C1—C2	1.397 (3)	O1—N1	1.258 (2)
C2—C3	1.383 (3)	N1—O2	1.228 (2)
C3—C4	1.383 (3)	N1—O3	1.236 (2)
C1—N2—H2	109.5	C5—C4—H5	119.9
C1—N2—H1	109.5	C3—C4—H5	119.9
H2—N2—H1	109.5	C4—C5—C6	121.21 (19)
C1—N2—H3	109.5	C4—C5—Cl	120.13 (17)
H2—N2—H3	109.5	C6—C5—Cl	118.66 (17)
H1—N2—H3	109.5	C1—C6—C5	118.04 (19)
C2—O4—C7	118.86 (18)	C1—C6—H6	121.0
C6—C1—C2	122.12 (18)	C5—C6—H6	121.0
C6—C1—N2	120.77 (18)	O4—C7—H7	109.5
C2—C1—N2	117.11 (17)	O4—C7—H8	109.5
O4—C2—C3	126.62 (19)	H7—C7—H8	109.5

O4—C2—C1	115.18 (18)	O4—C7—H9	109.5
C3—C2—C1	118.19 (19)	H7—C7—H9	109.5
C4—C3—C2	120.2 (2)	H8—C7—H9	109.5
C4—C3—H4	119.9	O2—N1—O3	120.9 (2)
C2—C3—H4	119.9	O2—N1—O1	120.0 (2)
C5—C4—C3	120.3 (2)	O3—N1—O1	119.02 (18)

C7—O4—C2—C3	12.4 (3)	C2—C3—C4—C5	0.8 (3)
C7—O4—C2—C1	−168.9 (2)	C3—C4—C5—C6	0.1 (3)
C6—C1—C2—O4	−178.65 (18)	C3—C4—C5—Cl	−179.46 (17)
N2—C1—C2—O4	1.4 (3)	C2—C1—C6—C5	0.7 (3)
C6—C1—C2—C3	0.2 (3)	N2—C1—C6—C5	−179.35 (18)
N2—C1—C2—C3	−179.74 (18)	C4—C5—C6—C1	−0.9 (3)
O4—C2—C3—C4	177.7 (2)	Cl—C5—C6—C1	178.71 (15)
C1—C2—C3—C4	−1.0 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···O1^{i}	0.89	2.08	2.967 (3)	173
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Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*+2, *y*+1/2, −*z*+3/2; (iii) *x*, *y*+1, *z*.

Fig. 1

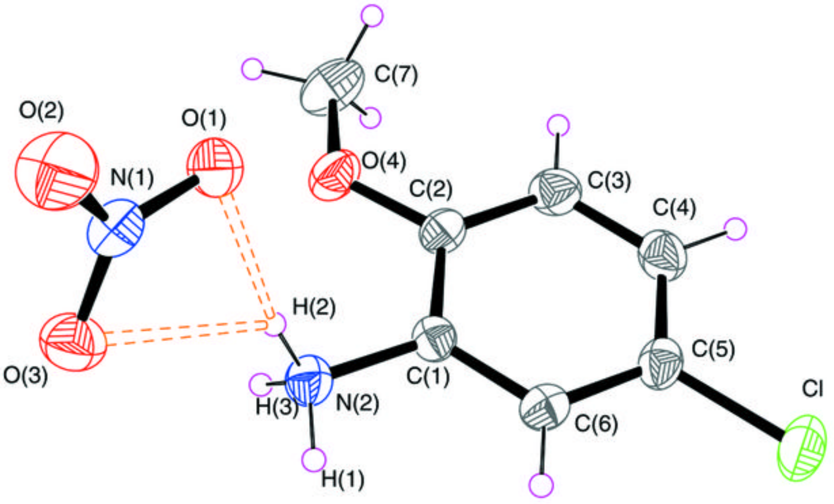


Fig. 2

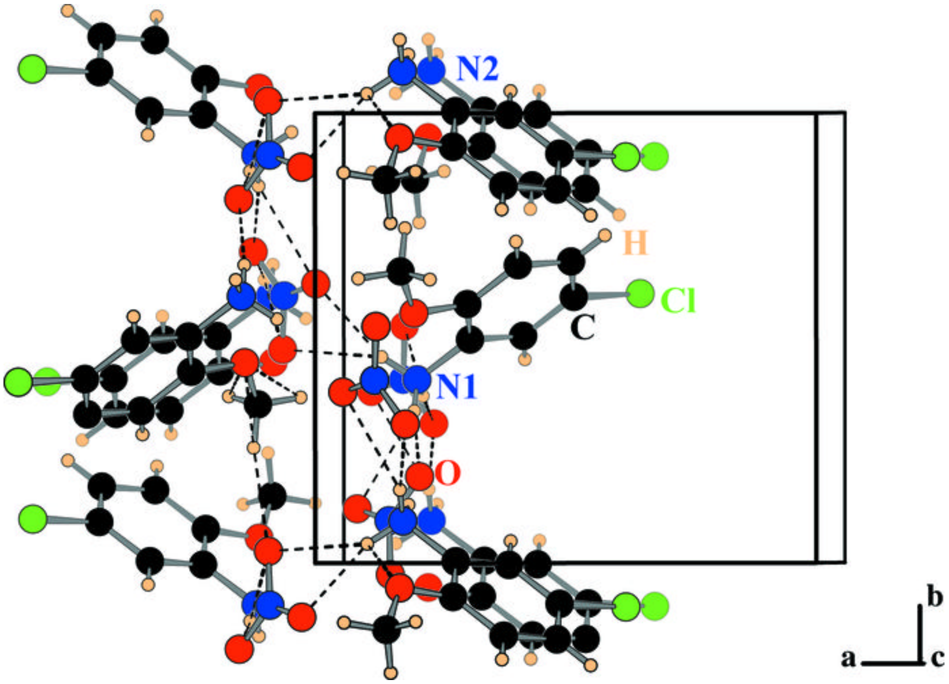
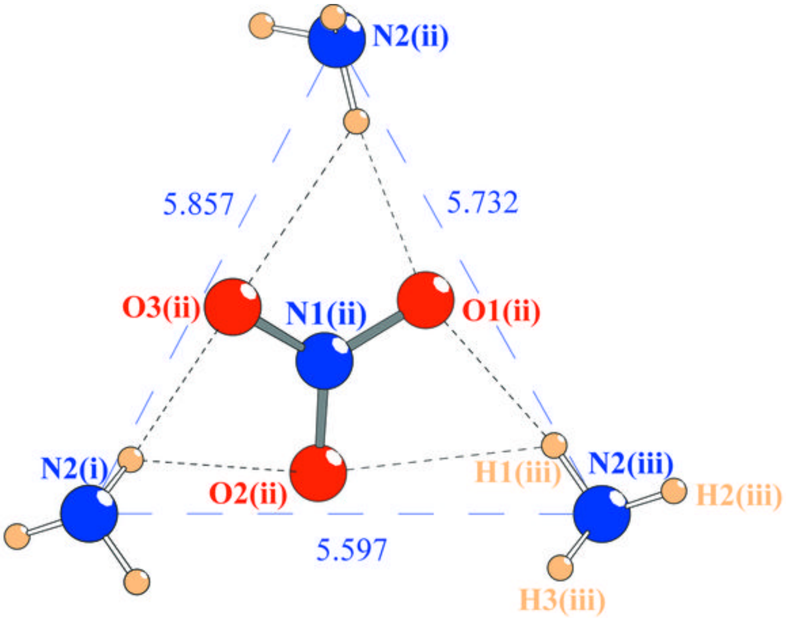


Fig. 3


N2(ii)
5.857
5.732
O3(ii)
N1(ii)
O1(ii)
N2(i)
O2(ii)
H1(iii)
N2(iii)
H2(iii)
5.597
H3(iii)